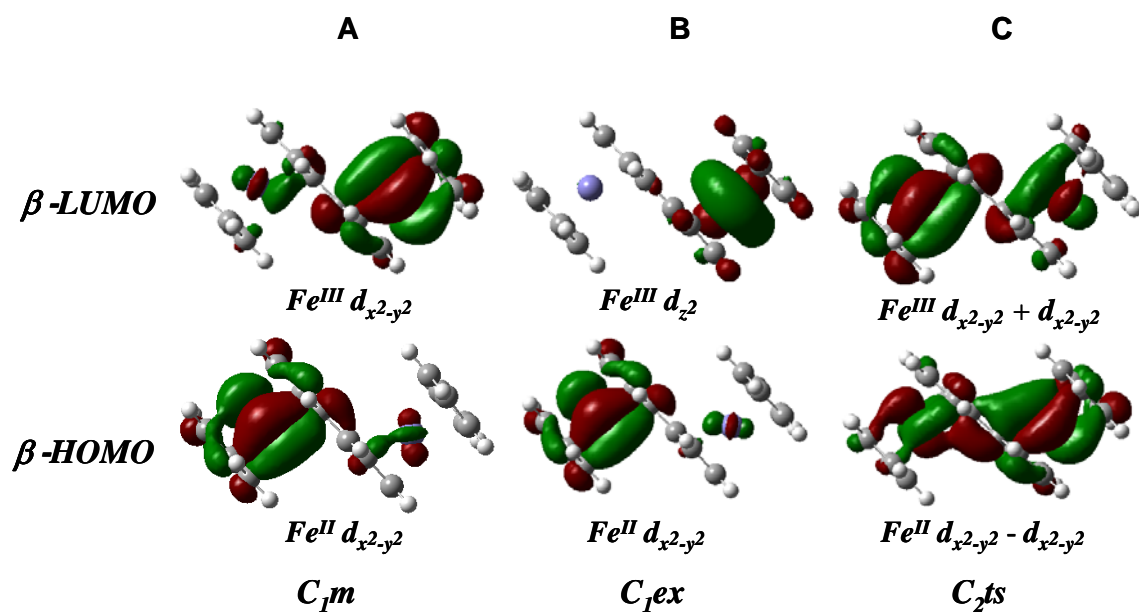


**Supporting Information for:**  
**Exploring the Ground and Excited State Potential Energy Landscapes of the Mixed-Valence**  
**Biferricenium Complex**

Ryan G. Hadt, Victor N. Nemykin,\*

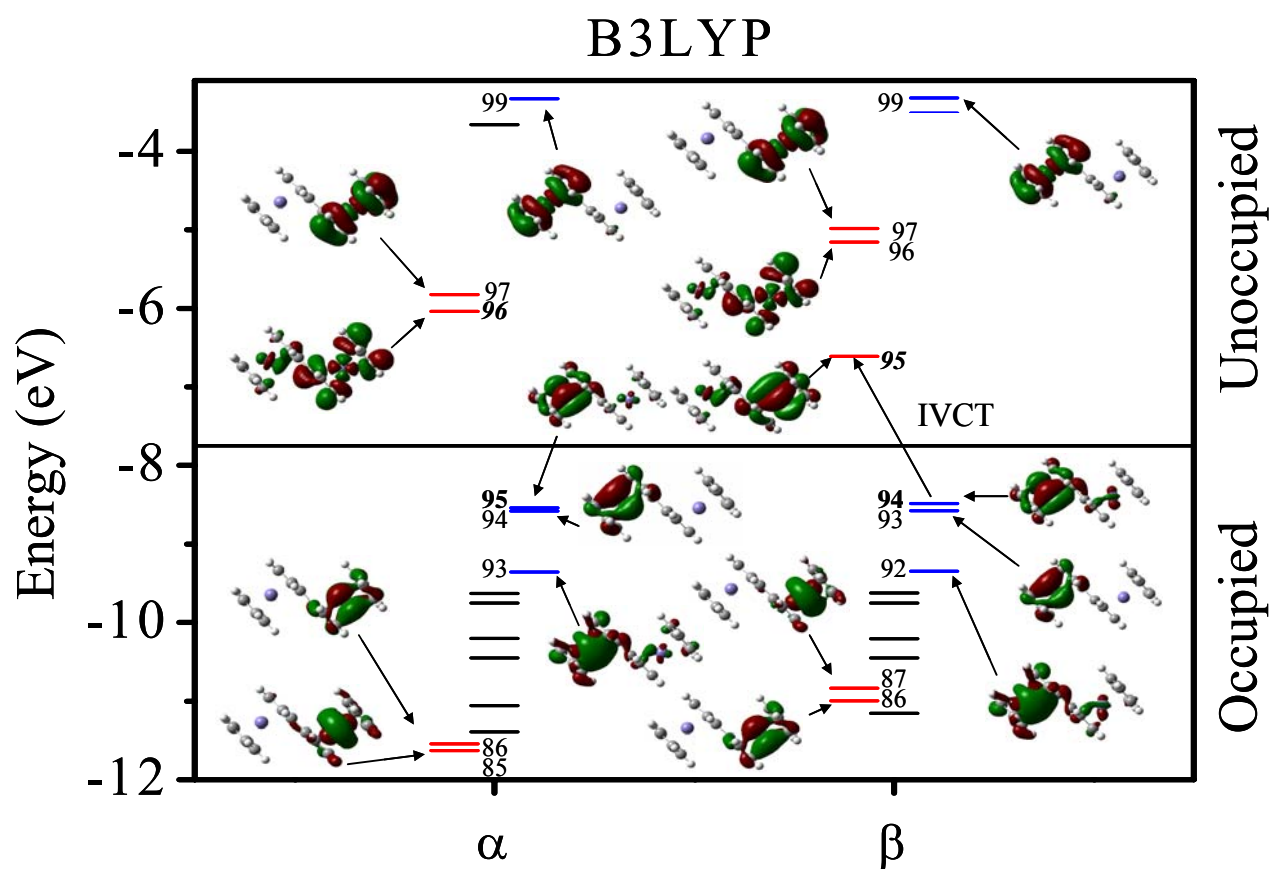
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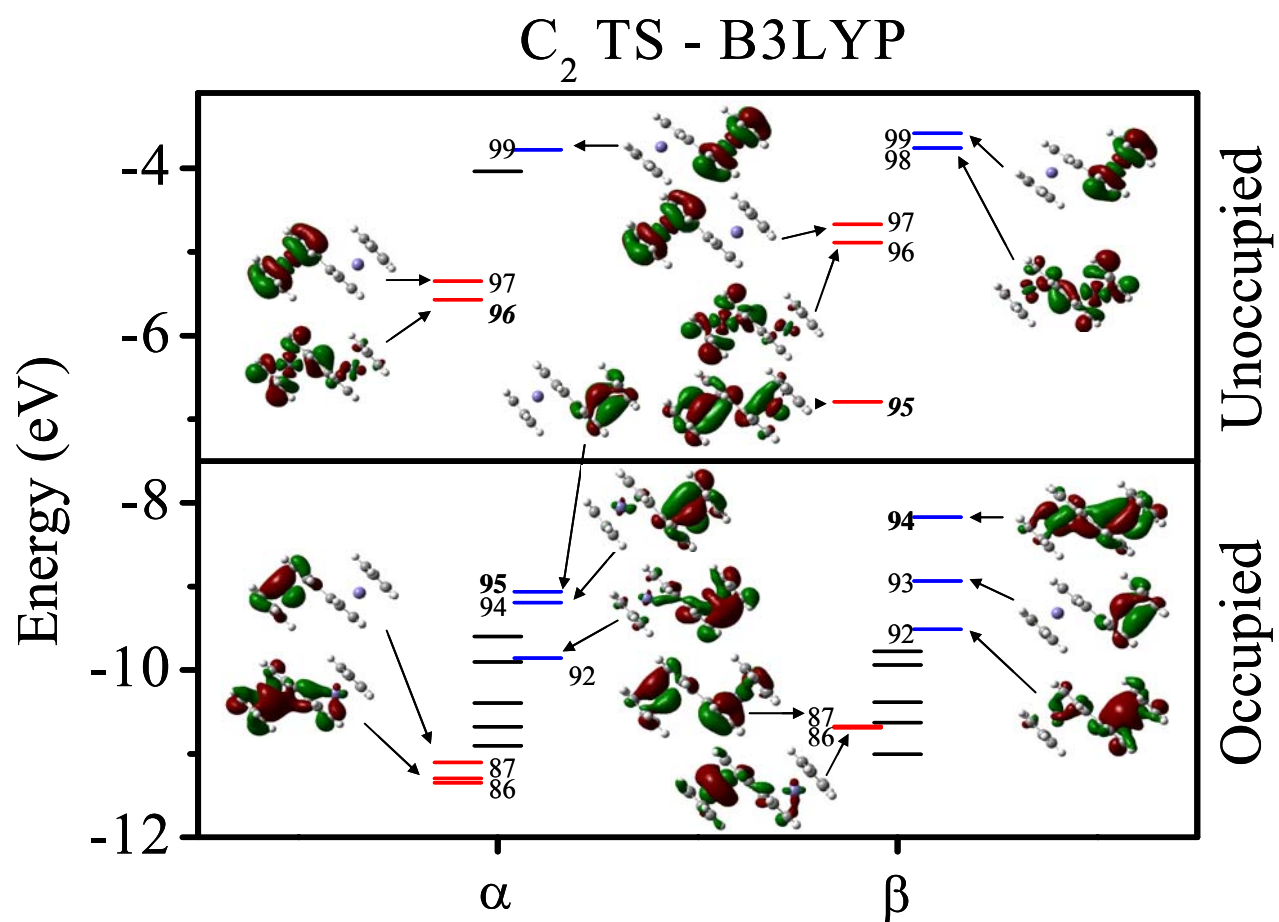


**Supporting Information Figure 1.**  $\beta$  HOMO and LUMO MOs for  $C_{1m}$  (A),  $C_{1ex}$  (B), and  $C_{2ts}$  (C)

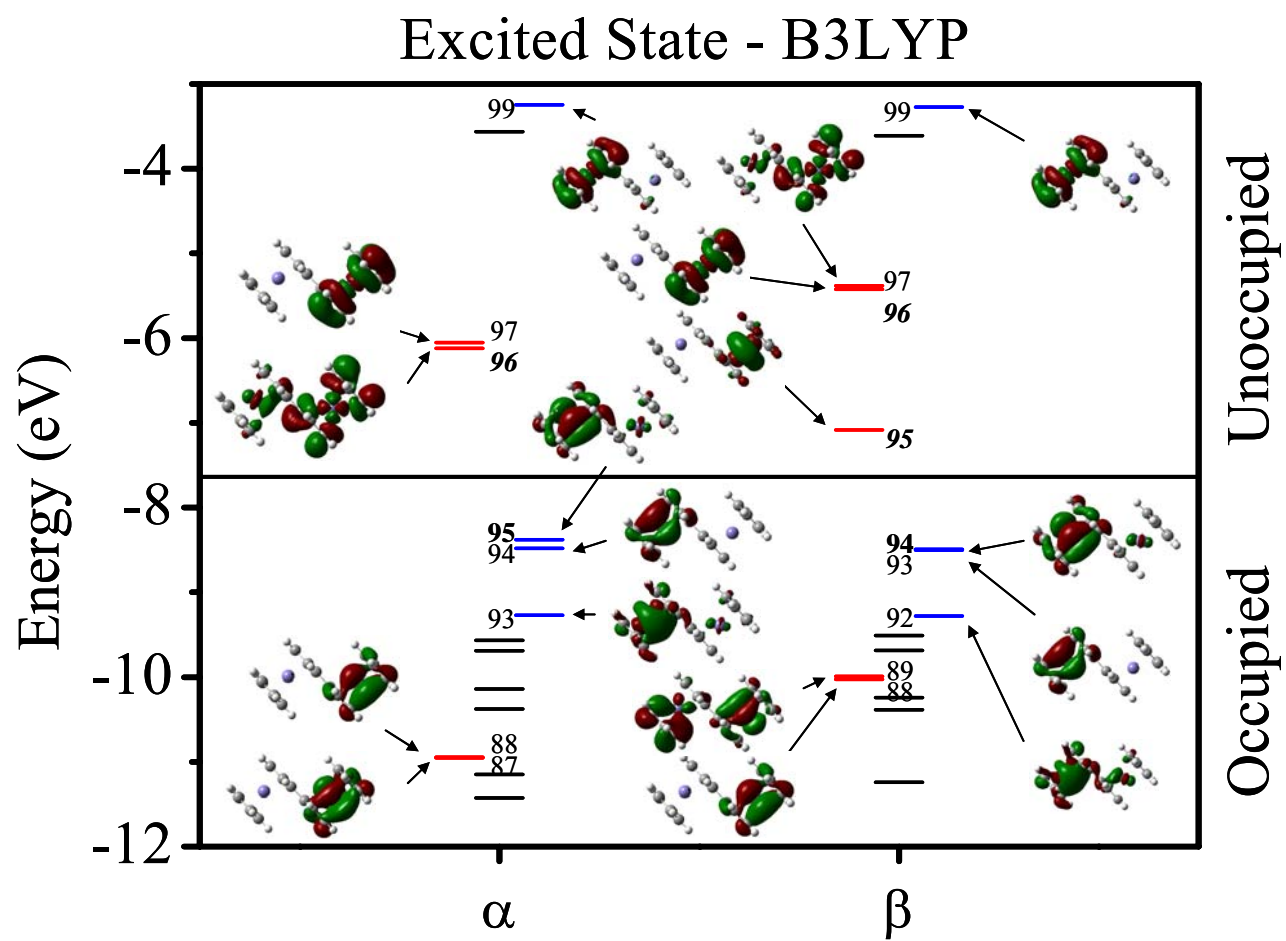
obtained using B3LYP exchange-correlation functional.



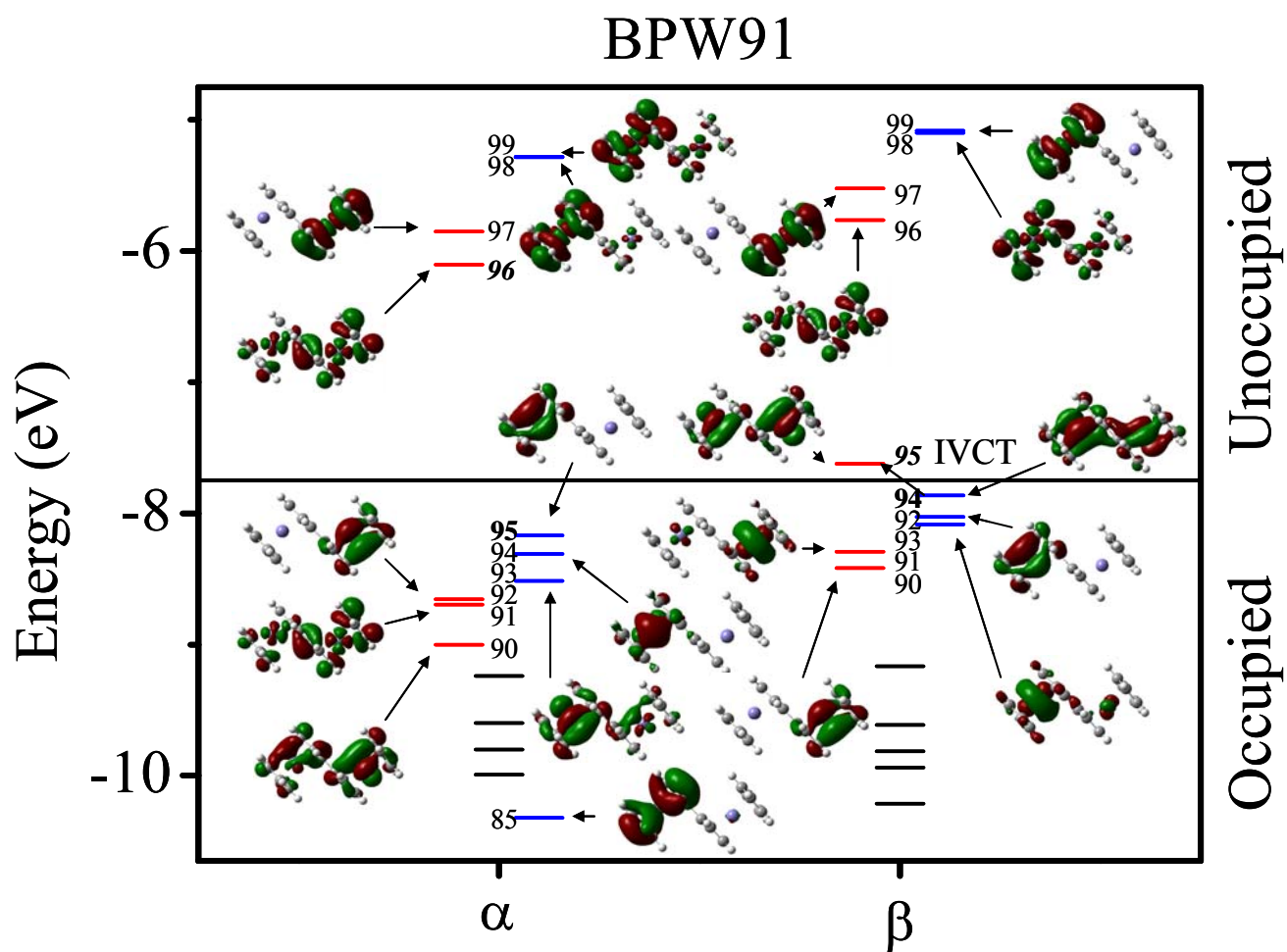
**Supporting Information Figure 2.** DFT predicted (B3LYP) molecular orbital diagram for **C<sub>1</sub>m**.



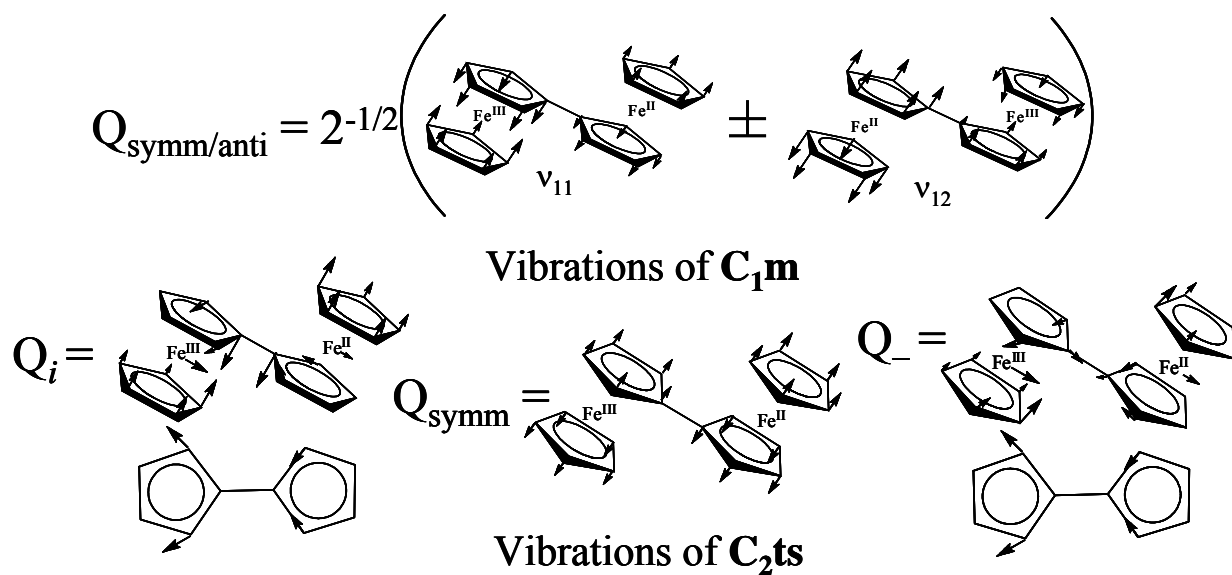
Supporting Information Figure 3. DFT predicted (B3LYP) molecular orbital diagram for  $C_2$ ts.



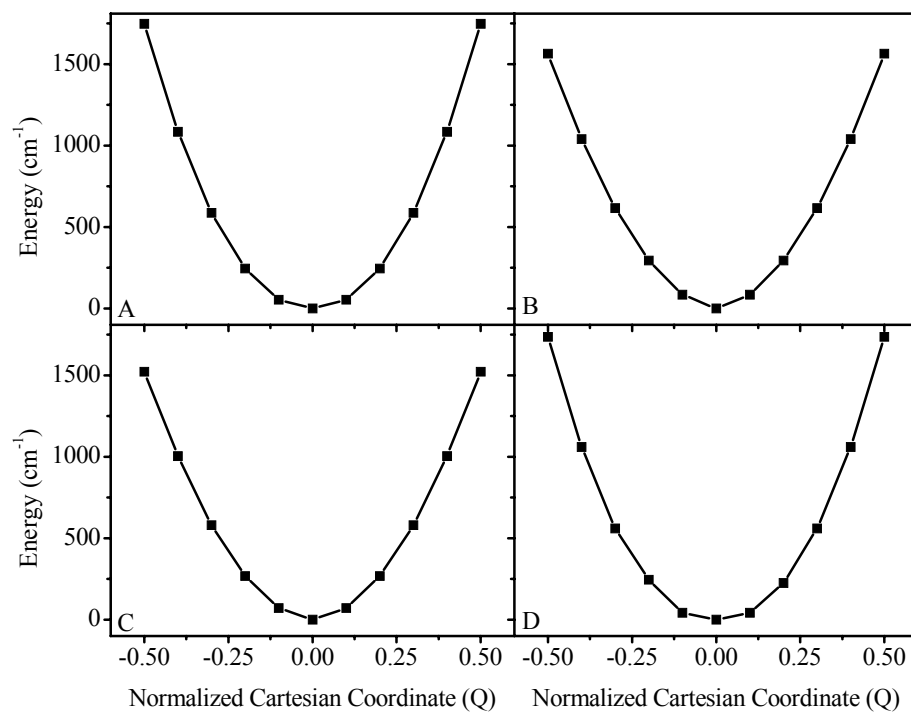
**Supporting Information Figure 4.** DFT predicted (B3LYP) molecular orbital diagram for **C<sub>1</sub>ex**.



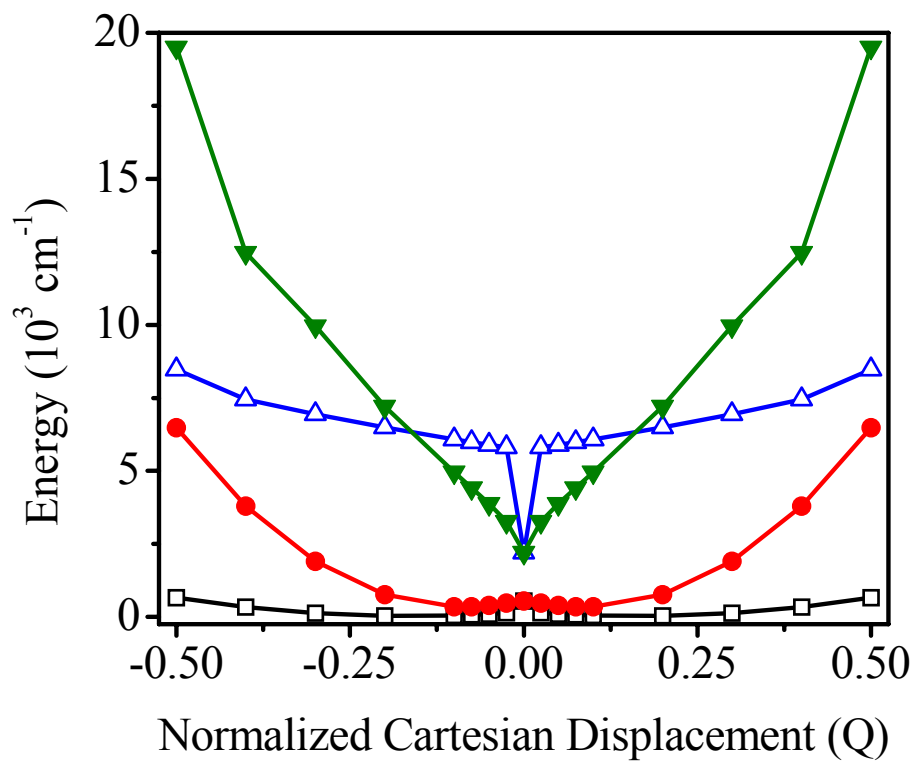
**Supporting Information Figure 5.** DFT predicted (BPW91) molecular orbital diagram for the  $C_{1m}$ .



**Supporting Information Figure 6.** Important vibrations for both  $C_{1m}$  and  $C_{2ts}$ . Arrows indicated relative amplitude of vibration.

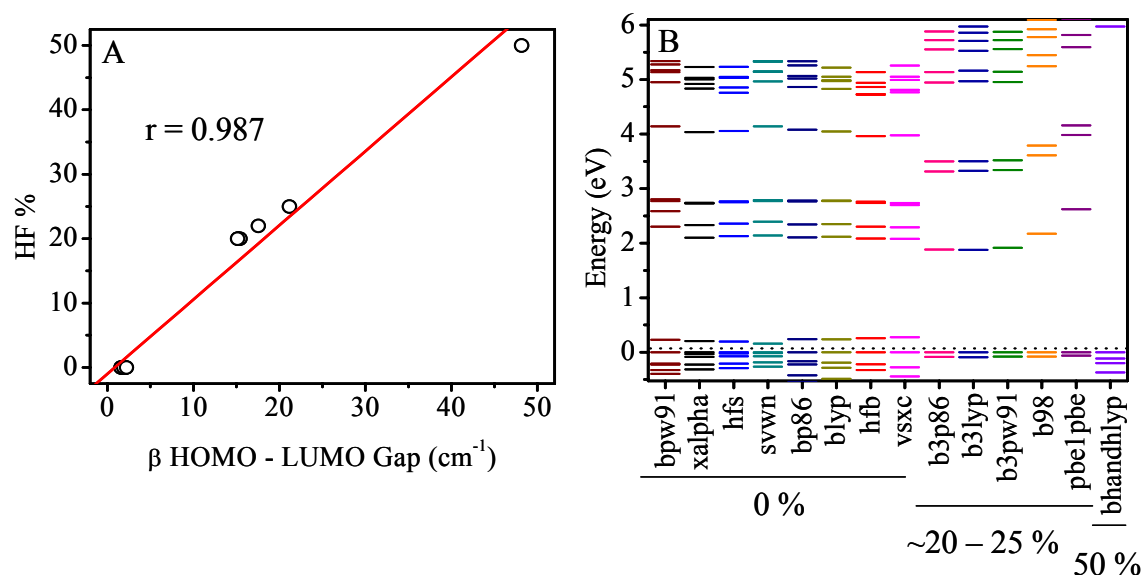


**Supporting Information Figure 7.** Important DFT (B3LYP) predicted PESs for the  $C_{1m}$  geometry: (A)  $v_{11}$ ; (B)  $v_{12}$ ; (C)  $Q_{\text{symm}}$  and (D)  $Q_{\text{anti}}$ .

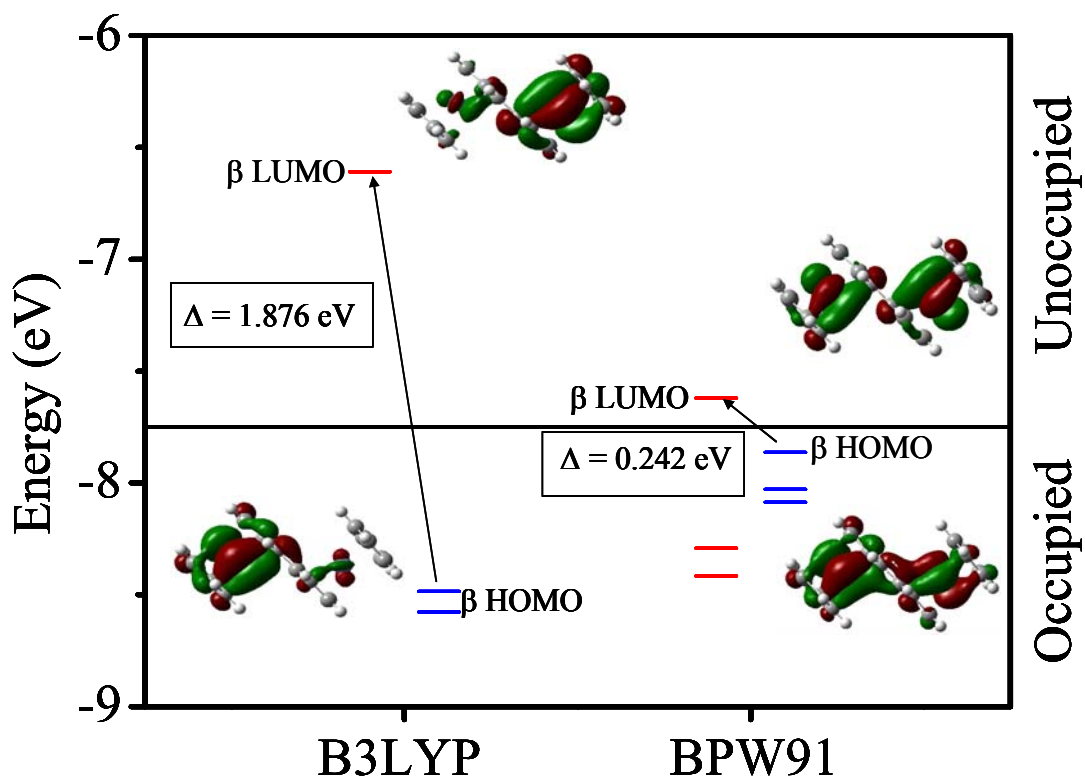


**Supporting Information Figure 8.** DFT and TDDFT predicted lower and upper adiabatic relaxed (black and blue) and rigid (red and green) PESs for the  $\text{BF}^+$  cation.

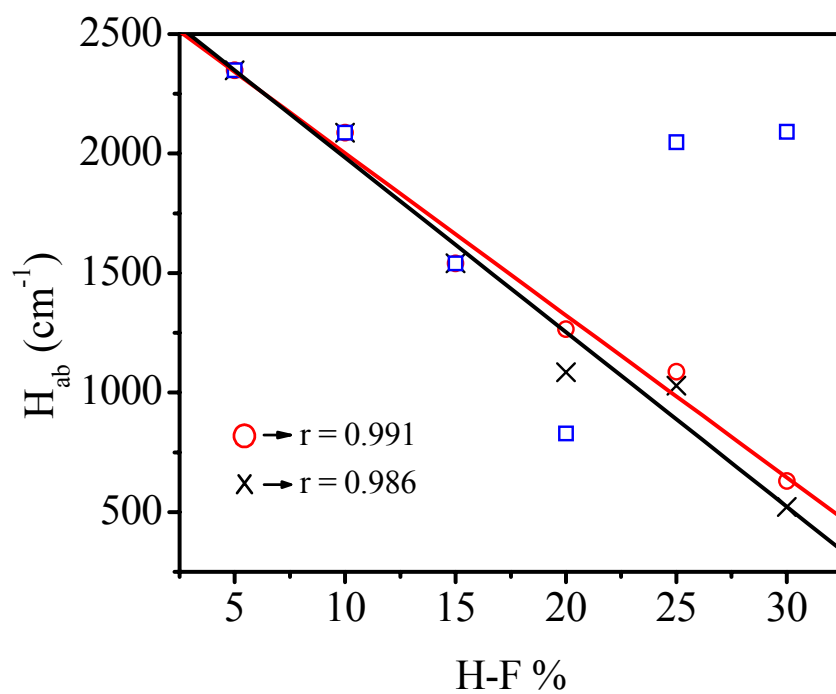




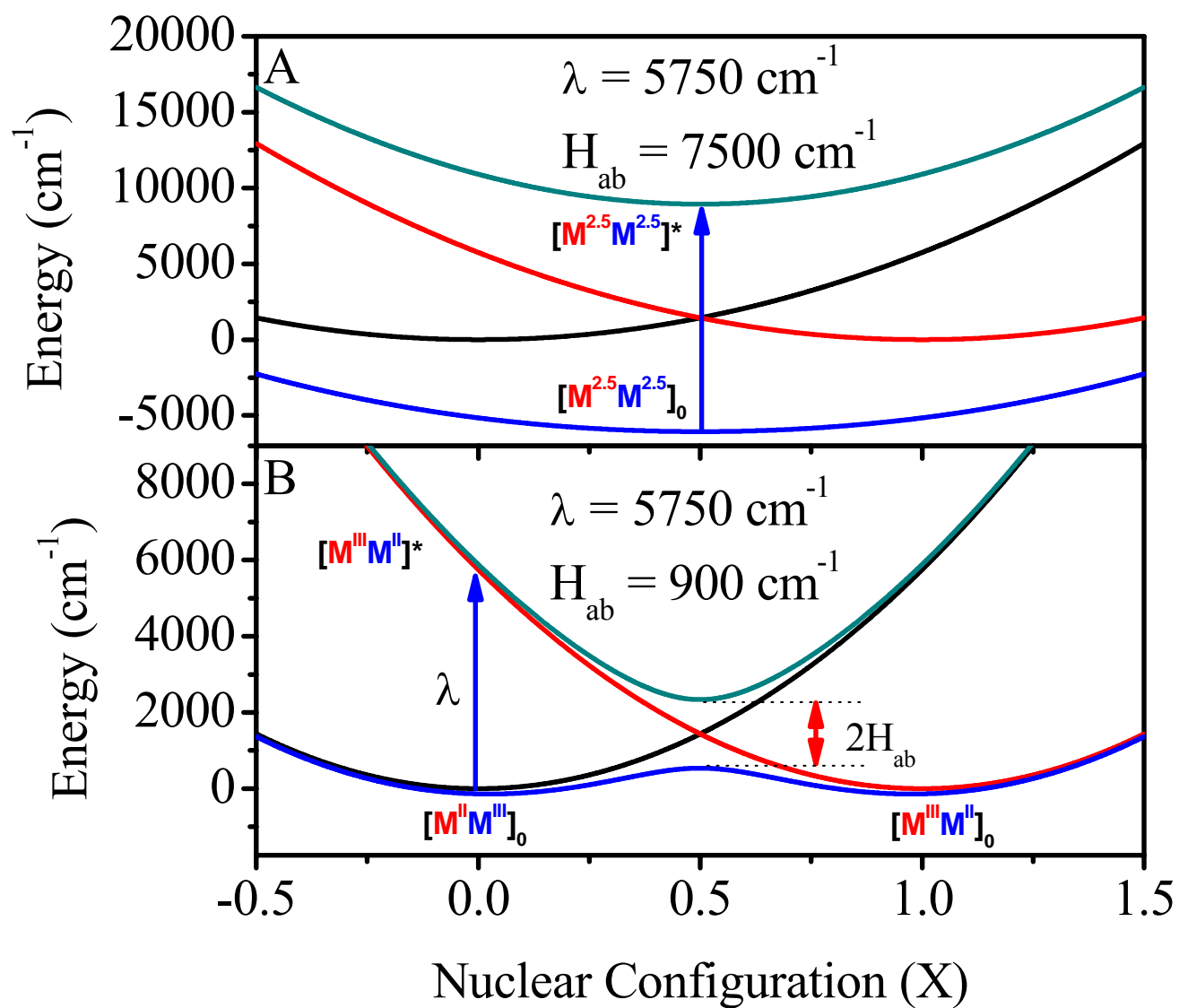
**Supporting Information Figure 9.**  $\beta$  HOMO-LUMO gap dependence: (A) correlation between Hartree-Fock percentage (B) partial MO diagram for 14 different exchange correlation functionals.



**Supporting Information Figure 10.**  $\beta$  HOMO-LUMO gap and MO plots for B3LYP and BPW91.



**Supporting Information Figure 11.** Linear dependence of  $H_{ab}$  evaluated using Methods I (blue squares), IIA (black x's), and IIIB (red circles) for 5, 10, 15, 20, 25, and 30 % of Hartree-Fock exchange.



**Supporting Information Figure 12.** Class III (A) *versus* class II (B) PES profiles with various values of  $H_{ab}$ .

**Supporting Information Table 1.** Important structural parameters of **BF** and **BF<sup>+</sup>** (Å and degree) obtained via B3LYP optimization.

Symm.	Fe-Fe	Fe <sup>2.5</sup> -C <sub>i</sub>	Fe <sup>II</sup> -C <sub>i</sub>	Fe <sup>III</sup> -C <sub>i</sub>	C <sub>i</sub> -C <sub>i</sub>	θ <sub>FeII</sub>	θ <sub>FeIII</sub>	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>	r <sub>4</sub>
<b>Neutral</b>											
C <sub>2h</sub> <sup>a</sup>	5.209		2.098		1.466	0.0		2.080	2.081	2.081	2.080
exp <sup>b</sup>	5.112		2.062		1.459	14.4		2.051	2.056	2.056	2.051
<b>Mixed-valent</b>											
<b>Gas-Phase</b>											
<b>C<sub>1m</sub></b> <sup>a</sup>	5.278		2.074	2.229	1.446	2.5	4.5	2.135	2.127	2.081	2.084
exp <sup>c</sup>	5.082		2.041	2.114	1.450	4.5	18.3	2.030	2.056	2.072	2.072
C <sub>1</sub> <sup>d</sup>	5.274		2.074	2.227	1.445	0.1	22.4	2.133	2.130	2.081	2.084
C <sub>1</sub> <sup>e</sup>	5.279		2.076	2.225	1.445	22.2	22.3	2.087	2.083	2.128	2.136
<b>C<sub>1ex</sub></b>	5.228		2.072	2.168	1.449	2.8	3.5	2.105	2.105	2.080	2.084
<b>C<sub>2ts</sub></b>	5.253	2.146			1.445	3.0	3.0	2.109	2.099	2.109	2.099
C <sub>i</sub>	5.251	2.145			1.445	3.4	-3.4	2.110	2.098	2.098	2.110
C <sub>2h</sub> <sup>f</sup>	5.250	2.145			1.445	0.0	0.0	2.109	2.098	2.098	2.109
C <sub>2h</sub> <sup>g</sup>	5.252	2.144			1.445	0.0	0.0	2.112	2.099	2.099	2.112
<b>CH<sub>2</sub>Cl<sub>2</sub></b>											
<b>C<sub>1m</sub></b>	5.272		2.077	2.212	1.453	2.4	4.2	2.081	2.080	2.124	2.129
<b>C<sub>2ts</sub></b>	5.235	2.141			1.444	3.0	3.0	2.107	2.096	2.096	2.107
<b>CH<sub>3</sub>CN</b>											
<b>C<sub>1m</sub></b>	5.272		2.076	2.212	1.453	2.4	4.2	2.081	2.080	2.124	2.129
<b>C<sub>2ts</sub></b>	5.232	2.140			1.444	3.0	3.0	2.107	2.096	2.096	2.107

<sup>a</sup>Global minima; <sup>b</sup> CCDC code: BIFERO02; <sup>c</sup> CCDC code: FEKFUW; <sup>d</sup> single D<sub>5d</sub> and single D<sub>5h</sub> Cp conformations; <sup>e</sup> 2 D<sub>5h</sub> Cp conformations; <sup>a</sup> 2 D<sub>5h</sub> Cp conformations; <sup>g</sup> 2 D<sub>5d</sub> Cp conformations.

**Supporting Information Table 2.** DFT (B3LYP) predicted molecular orbitals with significant d character for the **C<sub>1</sub>m** geometry (HOMO in bold and LUMO in bold and italics).

$\alpha$ set							$\beta$ set						
MO	Type	Energy (eV)	Fe <sup>III</sup>	Fe <sup>II</sup>	Cp <sup>III</sup>	Cp <sup>II</sup>	MO	Type	Energy (eV)	Fe <sup>III</sup>	Fe <sup>II</sup>	Cp <sup>III</sup>	Cp <sup>II</sup>
82	d <sub>x2-y2</sub>	-12.369	68.6	0.9	23.4	7.1	82	cpd <sub>xz</sub>	-11.938	24.1	2.9	53.5	17.5
83	cpd <sub>xz</sub>	-12.236	58.8	0.6	36.4	4.1	83	cpd <sub>yz</sub>	-11.818	32.1	0.0	67.6	0.2
84	cpd <sub>yz</sub>	-12.196	43.4	0.0	56.4	0.2	86	d <sub>xy</sub>	-10.998	78	0	21.7	0.3
85	d <sub>z2</sub>	-11.630	92.3	0.1	6.6	0.9	87	d <sub>z2</sub>	-10.834	91.7	0.1	7.5	0.7
86	d <sub>xy</sub>	-11.543	81.7	0	17.8	0.5	88	cpd <sub>yz</sub>	-10.451	0.1	25.7	0.9	73.3
89	cpd <sub>yz</sub>	-10.451	0.1	25.8	1.1	73.0	89	cpd <sub>xz</sub>	-10.205	3.1	26.7	13.4	56.9
90	cpd <sub>xz</sub>	-10.204	3.1	26.4	14.0	56.5	92	d <sub>z2</sub>	-9.346	1.5	80.1	4.5	13.9
93	d <sub>z2</sub>	-9.357	1.6	80.4	4.2	13.8	93	d <sub>xy</sub>	-8.576	0	73.3	0.5	26.1
94	d <sub>xy</sub>	-8.582	0	73.5	0.5	25.9	<b>94</b>	<b>d<sub>x2-y2</sub></b>	<b>-8.485</b>	<b>1.8</b>	<b>61.3</b>	<b>3.6</b>	<b>33.3</b>
<b>95</b>	<b>d<sub>x2-y2</sub></b>	<b>-8.540</b>	<b>1.6</b>	<b>62.8</b>	<b>2.2</b>	<b>33.4</b>	<b>95</b>	<b>cpd<sub>x2-y2</sub></b>	<b>-6.609</b>	<b>49.2</b>	<b>3.1</b>	<b>44.3</b>	<b>3.4</b>
<b>96</b>	<b>cpd<sub>xz</sub></b>	<b>-6.036</b>	<b>38.5</b>	<b>3.8</b>	<b>53.1</b>	<b>4.6</b>	96	cpd <sub>xz</sub>	-5.159	46.4	2.8	47.1	3.7
97	cpd <sub>yz</sub>	-5.825	41.1	0.1	58	0.8	97	cpd <sub>yz</sub>	-4.982	46.1	0.1	52.8	1
99	cpd <sub>yz</sub>	-3.334	0.3	41.2	3.7	54.8	99	cpd <sub>yz</sub>	-3.324	0.1	25.7	0.9	73.3

**Supporting Information Table 3.** DFT (B3LYP) predicted molecular orbitals with significant d character for the optimized **C<sub>2</sub>ts** geometry (HOMO in bold and LUMO in bold and italics).

$\alpha$ -set							$\beta$ -set						
MO	Type	Energy (eV)	Fe <sup>III</sup>	Fe <sup>II</sup>	Cp <sup>III</sup>	Cp <sup>II</sup>	MO	Type	Energy (eV)	Fe <sup>III</sup>	Fe <sup>II</sup>	Cp <sup>III</sup>	Cp <sup>II</sup>
82	cpd <sub>xz</sub>	-12.138	41.9	2.2	43.3	12.5	82	cpd <sub>xz</sub>	-11.889	22.5	3.4	53.9	20.2
83	cpd <sub>yz</sub>	-11.926	40.4	0.0	59.2	0.3	83	cpd <sub>yz</sub>	-11.651	31.8	0.0	67.9	0.3
84	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	-11.783	75.5	0.2	23.2	1.0	86	d <sub>z<sup>2</sup></sub>	-10.686	87.9	0.9	8.0	3.2
86	cpd <sub>z<sup>2</sup></sub>	-11.296	67.1	2.1	21.2	9.6	87	d <sub>xy</sub>	-10.672	60.8	5.7	17.0	16.5
87	d <sub>xy</sub>	-11.102	79.1	0.0	20.4	0.5	88	cpd <sub>yz</sub>	-10.625	25.3	17.6	10.7	46.4
89	cpd <sub>yz</sub>	-10.676	0.6	28.1	4.8	66.4	89	cpd <sub>xz</sub>	-10.383	6.0	27.8	13.5	52.7
90	cpd <sub>xz</sub>	-10.394	2.3	27.9	14.4	55.4	92	d <sub>z<sup>2</sup></sub>	-9.511	2.8	73.3	6.4	17.5
92	d <sub>z<sup>2</sup></sub>	-9.856	1.2	67.1	5.5	26.3	93	d <sub>xy</sub>	-8.935	0.0	72.7	0.3	27.0
94	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	-9.194	0.9	67.8	2.1	29.2	<b>94</b>	<b>d<sub>x<sup>2</sup>-y<sup>2</sup></sub> - d<sub>x<sup>2</sup>-y<sup>2</sup></sub></b>	<b>-8.172</b>	<b>9.6</b>	<b>46.5</b>	<b>12.2</b>	<b>31.7</b>
<b>95</b>	<b>d<sub>xy</sub></b>	<b>-9.061</b>	<b>0.0</b>	<b>74.8</b>	<b>0.4</b>	<b>24.8</b>	<b>95</b>	<b>d<sub>x<sup>2</sup>-y<sup>2</sup></sub> + d<sub>x<sup>2</sup>-y<sup>2</sup></sub></b>	<b>-6.791</b>	<b>42.2</b>	<b>12.2</b>	<b>36.1</b>	<b>9.4</b>
<b>96</b>	<b>cpd<sub>xz</sub></b>	<b>-5.570</b>	<b>40.5</b>	<b>3.7</b>	<b>50.2</b>	<b>5.5</b>	96	cpd <sub>xz</sub>	-4.890	45.0	3.1	48.9	3.0
97	cpd <sub>yz</sub>	-5.350	41.3	0.1	57.8	0.8	97	cpd <sub>yz</sub>	-4.671	44.9	0.1	54.0	1.0
98	cpd <sub>xz</sub>	-4.039	3.2	35.9	26.2	34.8	98	cpd <sub>xz</sub>	-3.758	3.4	41.4	15.0	40.2
99	cpd <sub>yz</sub>	-3.779	0.3	42.3	2.2	55.2	99	cpd <sub>yz</sub>	-3.582	0.3	42.6	2.9	54.2

**Supporting Information Table 4.** DFT (B3LYP) predicted molecular orbitals with significant d character for the optimized **C<sub>1</sub>ex** geometry (HOMO in bold and LUMO in bold and italics).

$\alpha$ -set							$\beta$ -set						
MO	Type	Energy (eV)	Fe <sup>III</sup>	Fe <sup>II</sup>	Cp <sup>III</sup>	Cp <sup>II</sup>	MO	Type	Energy (eV)	Fe <sup>III</sup>	Fe <sup>II</sup>	Cp <sup>III</sup>	Cp <sup>II</sup>
79	d <sub>z2</sub>	-13.164	88.8	0.7	7.2	3.2	82	cpd <sub>yz</sub>	-12.250	36.7	0.0	63	0.3
83	cpd <sub>yz</sub>	-12.486	44.6	0.0	54.7	0.6	83	cpd <sub>xz</sub>	-12.105	28.7	2.2	54.7	14.4
84	cpd <sub>xz</sub>	-12.453	39.1	1.8	44.6	14.5	86	cpd <sub>yz</sub>	-10.388	0.2	25.5	0.8	73.5
87	d <sub>xy</sub>	-10.953	75.5	0.0	24	0.5	87	cpd <sub>xz</sub>	-10.241	25.9	14.7	26.2	33.2
88	d <sub>x2-y2</sub>	-10.945	73.7	0.1	25.9	0.3	88	d <sub>xy</sub>	-10.029	69.2	0.1	30	0.7
89	cpd <sub>yz</sub>	-10.376	0.1	25.3	1	73.6	89	cpd <sub>x2-y2</sub>	-9.992	46.4	8.9	21	23.7
90	cpd <sub>xz</sub>	-10.141	4.3	26.2	12.9	56.6	92	d <sub>z2</sub>	-9.281	3.4	75.7	4.7	16.2
93	d <sub>z2</sub>	-9.268	1.3	83.3	3.4	12	93	d <sub>xy</sub>	-8.500	0	73.4	0.7	25.8
94	d <sub>xy</sub>	-8.479	0.0	73.1	0.7	26.2	<b>94</b>	<b>d<sub>x2-y2</sub></b>	<b>-8.493</b>	<b>1.4</b>	<b>63.7</b>	<b>1.6</b>	<b>33.3</b>
<b>95</b>	<b>d<sub>x2-y2</sub></b>	<b>-8.379</b>	<b>2.0</b>	<b>60.9</b>	<b>2.6</b>	<b>34.4</b>	<b>95</b>	<b>d<sub>z2</sub></b>	<b>-7.084</b>	<b>84.9</b>	<b>0.2</b>	<b>13.4</b>	<b>1.5</b>
<b>96</b>	<b>cpd<sub>xz</sub></b>	<b>-6.122</b>	<b>36.4</b>	<b>4.0</b>	<b>55.1</b>	<b>4.5</b>	96	cpd <sub>xz</sub>	-5.423	43.7	0.1	55.4	0.8
97	cpd <sub>yz</sub>	-6.052	39.0	0.1	60.2	0.7	97	cpd <sub>yz</sub>	-5.382	44.1	2.8	49.2	3.9
99	cpd <sub>yz</sub>	-3.244	0.4	40.5	5.1	54.1	99	cpd <sub>yz</sub>	-3.270	0.3	40.6	4.9	54.2

**Supporting Information Table 5.** DFT calculated (BPW91) quadrupole splittings, isomer shifts, and spin densities in various electric fields for the B3LYP optimized **C<sub>1m</sub>** localized minimum geometry.

field (a.u.)	$\Delta E_q$ (mm/s)	$\eta$	$\delta$ (mm/s)	spin density
<i>Neutral (C<sub>2h</sub>)</i>				
none	2.533	0.010	0.419	
exptl <sup>a</sup>	2.36		0.52	
<i>Average-Valence (C<sub>2ts</sub>)</i>				
none	1.512	0.606	0.410	0.601
	1.512	0.606	0.410	0.601
exptl <sup>b</sup>	1.130		0.505	
<i>Localized Mixed-Valence (C<sub>1m</sub>)</i>				
	Fe <sup>II</sup> /Fe <sup>III</sup>	Fe <sup>II</sup> /Fe <sup>III</sup>	Fe <sup>II</sup> /Fe <sup>III</sup>	Fe <sup>II</sup> /Fe <sup>III</sup>
none	1.622/1.281	0.494/0.427	0.382/0.438	0.457/0.758
0.0020	1.829/1.053	0.402/0.527	0.391/0.427	0.358/0.856
0.0025	1.880/0.999	0.382/0.556	0.393/0.424	0.334/0.879
0.0030	1.929/0.945	0.362/0.586	0.395/0.422	0.310/0.903
0.0035	1.978/0.894	0.342/0.617	0.397/0.419	0.285/0.926
0.0040	2.025/0.843	0.324/0.648	0.399/0.417	0.262/0.949
0.0045	2.071/0.795	0.305/0.678	0.401/0.414	0.238/0.971
0.0050	2.116/0.750	0.287/0.706	0.403/0.412	0.215/0.992
0.0055	2.159/0.707	0.270/0.729	0.405/0.409	0.193/1.013
0.0060	2.200/0.667	0.252/0.746	0.407/0.407	0.171/1.033
exptl <sup>b</sup>	2.141/0.288		0.510/0.518	

<sup>a</sup> ref. 48; <sup>b</sup> ref. 10.



**Supporting Information Table 6.** The calculated values of  $H_{ab}$ , the IVCT band, and oscillator strengths using various methods.

symm	HF %	imaginary freq (cm <sup>-1</sup> )	$\Delta E$ (cm <sup>-1</sup> )	IVCT (cm <sup>-1</sup> )	$f$	$H_{ab}^k$	$H_{ab}^l$	$H_{ab}^m$
<i>Gas-Phase</i>								
C <sub>2</sub>	5 <sup>a</sup>			4700	0.0355	2350		
C <sub>2</sub>	10 <sup>b</sup>			4180	0.0577	2090		
C <sub>2</sub>	15 <sup>c</sup>			3080	0.0717	1540		
C <sub>1</sub>	20 <sup>d</sup>		538	6490	0.0046		1080	1260
C <sub>2</sub>	20 <sup>d</sup>	642 B		1660	0.0658	830		
C <sub>1</sub>	25 <sup>e</sup>		688	6870	0.0001		1030	1090
C <sub>2</sub>	25 <sup>e</sup>	23 B		4100	0.0070	2050		
C <sub>1</sub>	30 <sup>f</sup>		728	5000	0.0004		520	630
C <sub>2</sub>	30 <sup>f</sup>	26 B		4180	0.0015	2090		
C <sub>1</sub>	21.98 <sup>g</sup>		659	7570	0.0011		1230	1360
C <sub>2</sub>	21.98 <sup>g</sup>			3600	0.0303	1800		
C <sub>1</sub>	25 <sup>h</sup>		776	8850	0.0021		1440	1550
C <sub>2</sub>	25 <sup>h</sup>	22 B		4940	0.0227	2470		
<i>Solution</i>								
C <sub>1</sub> <sup>i</sup>	20		672	9140	0.0011		1610	870
C <sub>2</sub> <sup>i</sup>	20			5920	0.0106	2970		
C <sub>1</sub> <sup>j</sup>	20		670	8910	0.0015		1560	670
C <sub>2</sub> <sup>j</sup>	20			6120	0.0106	3060		

<sup>a</sup> B3LYP-5; <sup>b</sup> B3LYP-10; <sup>c</sup> B3LYP-15; <sup>d</sup> B3LYP; <sup>e</sup> B3LYP-25; <sup>f</sup> B3LYP-30; <sup>g</sup> B98; <sup>h</sup> PBE1PBE;  
<sup>i</sup> CH<sub>2</sub>Cl<sub>2</sub>; <sup>j</sup> CH<sub>3</sub>CN; <sup>k</sup> Method 1; <sup>l</sup> Method IIA; <sup>m</sup> Method IIB;

**Supporting Information Table 7.** Energetics results of various geometry optimizations of **BF<sup>+</sup>** complex.

Symm.	HF %	$\Delta E^{\text{n}}$ (cm <sup>-1</sup> )	ZPE (cm <sup>-1</sup> )	$\Delta E$ ZPE (cm <sup>-1</sup> ) <sup>n</sup>	Imaginary freqs (cm <sup>-1</sup> ), symmetry	Spin Density Fe <sup>III</sup> /Fe <sup>II</sup>
Gas-phase						
C <sub>1</sub>	20 <sup>a</sup>	540	69990	360		1.27/0.02
	25 <sup>b</sup>	690	70460	630		1.34/-0.01
	30 <sup>c</sup>	730	70920	620		1.41/-0.02
	~22 <sup>d</sup>	660	69790	540		1.30/0.01
	25 <sup>e</sup>	780	70760	670		1.31/0.01
C <sub>2</sub>	5 <sup>f</sup>		70340			0.61/0.61
	10 <sup>g</sup>		70400			0.63/0.63
	15 <sup>h</sup>		70450			0.65/0.65
	20 <sup>a</sup>		69810		642 B	0.98/0.34
	25 <sup>b</sup>		70400		23 B	1.24/0.07
	30 <sup>c</sup>		70810		26 B	1.30/0.06
	~22 <sup>d</sup>		69670			1.16/0.14
	25 <sup>e</sup>		70650		22 B	1.20/0.10
	0 <sup>i</sup>		67860			0.59/0.59
	0 <sup>j</sup>		68260			0.59/0.59
C <sub>2</sub>	0 <sup>k</sup>		68640			0.53/0.53
PCM						
C <sub>1</sub> <sup>l</sup>	20 <sup>a</sup>	1560	69960	1380		1.28/0.00
C <sub>2</sub> <sup>l</sup>	20 <sup>a</sup>		69780		635 B	1.21/0.04
C <sub>1</sub> <sup>m</sup>	20 <sup>a</sup>	1420	69960	1240		1.28/0.00
C <sub>2</sub> <sup>m</sup>	20 <sup>a</sup>		69780		640 B	1.21/0.04

<sup>a</sup> B3LYP; <sup>b</sup> B3LYP-25; <sup>c</sup> B3LYP-30; <sup>d</sup> B98; <sup>e</sup> PBE1PBE; <sup>f</sup> B3LYP-5; <sup>g</sup> B3LYP-10; <sup>h</sup> B3LYP-15; <sup>i</sup> BP86; <sup>j</sup> BPW91; <sup>k</sup> LSDA; <sup>l</sup> CH<sub>2</sub>Cl<sub>2</sub>; <sup>m</sup> CH<sub>3</sub>CN; <sup>n</sup> energy difference between C<sub>2</sub> (localized) and C<sub>1</sub> (delocalized) geometries at corresponding level of theory.

**Supporting Information Table 8.** DFT results (quadrupole splittings, electron densities on Fe,  $\beta$ -set HOMO-LUMO gaps, and spin densities) for 14 different exchange-correlation functionals using the B3LYP optimized  $C_{1m}$  geometry.

Functional (HF %)	$\Delta E_q$ (mm/s)	$\eta$	$\rho$	$\Delta\rho$	$\beta$ gap (cm <sup>-1</sup> )	spin density
	Fe <sup>II</sup> /Fe <sup>III</sup>	Fe <sup>II</sup> /Fe <sup>III</sup>	Fe <sup>II</sup> /Fe <sup>III</sup>			Fe <sup>II</sup> /Fe <sup>III</sup>
X $\alpha$ (0)	1.63/1.30	0.56/0.44	11574.06/ 11573.88	0.18	1660	0.49/0.81
LSDA (0)	1.59/1.34	0.57/0.41	11560.17/ 11559.98	0.19	2100	0.45/0.70
HFS (0)	1.62/1.32	0.55/0.42	11559.02/ 11558.84	0.17	1570	0.48/0.78
HFB (0)	1.69/1.29	0.43/0.38	11615.70/ 11615.54	0.16	2100	0.48/0.82
BP86 (0)	1.62/1.29	0.49/0.41	11619.84/ 11619.66	0.18	1930	0.45/0.75
BPW91 (0)	1.62/1.28	0.49/0.43	11615.84/ 11615.66	0.18	1960	0.46/0.76
BLYP (0)	1.65/1.32	0.43/0.35	11615.48/ 11615.31	0.17	1900	0.45/0.74
VSXC (0)	1.69/1.27	0.40/0.32	11605.18/ 11605.00	0.18	2220	0.51/0.87
B3P86 (20)	3.12/0.56	0.18/0.70	11615.98/ 11616.02	-0.04	15200	0.02/1.28
B3PW91 (20)	2.12/0.55	0.18/0.72	11612.74/ 11612.78	-0.04	15420	0.01/1.30
B3LYP (20)	3.19/0.56	0.17/0.54	11612.45/ 11612.50	-0.06	15130	0.02/1.27
B98 (21.98)	3.29/0.58	0.16/0.47	11610.98/ 11611.03	-0.05	17550	0.00/1.30
PBE1PBE (25)	3.30/0.58	0.15/0.53	11616.68/ 11616.73	-0.04	21160	-0.01/1.36
BH&HLYP (50)	4.40/1.01	0.08/0.06	11618.69/ 11618.82	-0.13	48160	-0.01/1.55

*Cartesian coordinates for the most important stationary points discussed in manuscript:*

***C<sub>2h</sub> Neutral Gas Phase***

Fe	-1.69025500	1.98173100	0.00000000
C	-0.00767300	1.58715100	1.15093300
C	-0.00489700	0.73285100	0.00000000
C	0.00767300	2.94241500	0.71248100
C	0.00767300	2.94241500	-0.71248100
H	-0.02572600	1.25912200	2.18028800
H	-0.00135000	3.81492100	1.35027500
H	-0.00135000	3.81492100	-1.35027500
C	-0.00767300	1.58715100	-1.15093300
H	-0.02572600	1.25912200	-2.18028800
C	-3.38653500	0.78108600	0.00000000
C	-3.38170300	1.61966700	1.15299000
C	-3.37321300	2.97617700	-0.71332600
C	-3.37321300	2.97617700	0.71332600
H	-3.36169100	-0.29928100	0.00000000
H	-3.36601200	1.28483000	2.18044800
H	-3.35074800	3.85019500	-1.34871800
H	-3.35074800	3.85019500	1.34871800
C	-3.38170300	1.61966700	-1.15299000
H	-3.36601200	1.28483000	-2.18044800
C	0.00489700	-0.73285100	0.00000000
C	0.00767300	-1.58715100	1.15093300
C	0.00767300	-1.58715100	-1.15093300
C	-0.00767300	-2.94241500	0.71248100
C	-0.00767300	-2.94241500	-0.71248100
Fe	1.69025500	-1.98173100	0.00000000
C	3.38170300	-1.61966700	1.15299000
C	3.37321300	-2.97617700	0.71332600
C	3.37321300	-2.97617700	-0.71332600
C	3.38170300	-1.61966700	-1.15299000
C	3.38653500	-0.78108600	0.00000000
H	3.36601200	-1.28483000	-2.18044800
H	3.35074800	-3.85019500	-1.34871800
H	3.35074800	-3.85019500	1.34871800
H	3.36601200	-1.28483000	2.18044800
H	3.36169100	0.29928100	0.00000000
H	0.02572600	-1.25912200	-2.18028800
H	0.00135000	-3.81492100	-1.35027500
H	0.00135000	-3.81492100	1.35027500
H	0.02572600	-1.25912200	2.18028800

***C<sub>1m</sub> Gas Phase***

H	2.54128400	-2.73653500	1.36609800
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C	1.95407500	-2.09543500	0.72443200
C	1.95199800	-2.09982300	-0.70166500
C	1.04684300	-1.08537000	1.15629500
C	1.04304900	-1.09179200	-1.13673200
H	2.53628200	-2.74548200	-1.34134200
C	0.41962100	-0.49565500	0.00945600
H	0.84301500	-0.82480500	2.18475600
H	0.83309800	-0.83979900	-2.16604300
C	-0.56585900	0.56222200	0.00689200
C	-1.16656900	1.16972900	-1.15575100
C	-1.17478200	1.17096200	1.16476100
C	-2.09572900	2.14461400	-0.71224800
H	-0.94961400	0.93107800	-2.18693700
C	-2.10091100	2.14535600	0.71340300
H	-0.96551200	0.93264100	2.19763100
H	-2.71703100	2.75852600	-1.34771900
H	-2.72690200	2.75970500	1.34385400
C	4.52279700	0.13072700	-0.83805500
C	3.65320600	1.23247700	-1.10514600
C	4.66087500	0.01821600	0.57731000
H	4.99975600	-0.49670100	-1.57704100
C	3.26534000	1.79699300	0.13976600
H	3.34310900	1.57627400	-2.08137300
C	3.87818500	1.04661700	1.17589300
H	5.24988100	-0.71854300	1.10428100
H	2.57881400	2.62083500	0.27575100
H	3.75346200	1.21195800	2.23669300
C	-4.56309600	-0.12203600	0.63683300
C	-4.49303400	-0.19647700	-0.78367900
C	-3.68454200	-1.10712400	1.17471100
H	-5.16351800	0.57239000	1.20654200
C	-3.56937500	-1.22581300	-1.12713500
H	-5.03114400	0.43186100	-1.47872000
C	-3.07332200	-1.78954200	0.08430500
H	-3.50809200	-1.29523800	2.22388100
H	-3.29349300	-1.52284200	-2.12860000
H	-2.34480300	-2.58432000	0.16234800
Fe	2.63728400	-0.27137600	-0.00037800
Fe	-2.61540800	0.24506500	-0.00023500

*C<sub>1m</sub> CH<sub>2</sub>Cl<sub>2</sub>*

H	2.56707500	-2.72451100	1.37584900
C	1.96279200	-2.09478500	0.73270100
C	1.95581800	-2.10266300	-0.69492500
C	1.05029700	-1.08975000	1.16645700
C	1.03872600	-1.10195300	-1.13040000

H	2.55281700	-2.74003800	-1.33724800
C	0.43232300	-0.49850800	0.01827300
H	0.85729000	-0.81984700	2.19872300
H	0.83153800	-0.84615100	-2.16343000
C	-0.56196000	0.56095100	0.01548400
C	-1.15399300	1.16909500	-1.14703000
C	-1.16961800	1.16609800	1.17140700
C	-2.09293100	2.13967900	-0.70671900
H	-0.92841600	0.92655600	-2.17841200
C	-2.10274600	2.13765000	0.72060200
H	-0.95928700	0.91984200	2.20517000
H	-2.71891300	2.74926500	-1.34708200
H	-2.73798700	2.74548400	1.35350100
C	4.50883300	0.13048200	-0.83885100
C	3.63704400	1.22834500	-1.11807900
C	4.64338900	0.03096800	0.57964800
H	4.97722100	-0.51544300	-1.57262800
C	3.24400800	1.80283500	0.12199300
H	3.31567600	1.55355400	-2.10122300
C	3.85747000	1.06401900	1.16735600
H	5.22174100	-0.71230100	1.11671400
H	2.55032600	2.62677300	0.25015200
H	3.71692000	1.22963000	2.23000500
C	-4.55711100	-0.12975500	0.63484200
C	-4.48606300	-0.19519000	-0.78858900
C	-3.67283600	-1.11613200	1.16671900
H	-5.15397300	0.56657600	1.21159900
C	-3.55673000	-1.22045700	-1.13807000
H	-5.02005900	0.44319300	-1.48231300
C	-3.05631300	-1.78944300	0.07091200
H	-3.48343000	-1.30358200	2.21677400
H	-3.26616300	-1.50252600	-2.14285500
H	-2.31670900	-2.57754500	0.14464400
Fe	2.63255300	-0.26797100	-0.00031600
Fe	-2.61440100	0.24613000	0.00030300

***C<sub>1m</sub> CH<sub>3</sub>CN***

H	2.56756100	-2.72297300	1.37456600
C	1.96265700	-2.09395600	0.73110100
C	1.95716500	-2.10078300	-0.69658300
C	1.04861300	-1.09029400	1.16471300
C	1.03925000	-1.10085400	-1.13240300
H	2.55621500	-2.73647800	-1.33886600
C	0.43150600	-0.49881900	0.01626000
H	0.85418600	-0.82095400	2.19701000
H	0.83302200	-0.84419000	-2.16557400

C	-0.56315600	0.56054700	0.01348500
C	-1.15518600	1.16878400	-1.14886500
C	-1.16964900	1.16647000	1.16958800
C	-2.09314700	2.14031500	-0.70836400
H	-0.93053900	0.92576200	-2.18045800
C	-2.10225200	2.13875800	0.71900400
H	-0.95889100	0.92024600	2.20338700
H	-2.71910300	2.75042900	-1.34842800
H	-2.73668100	2.74739900	1.35212200
C	4.50338200	0.13296600	-0.84561800
C	3.63266200	1.23497900	-1.11209500
C	4.64632900	0.02335300	0.57131100
H	4.96502600	-0.50959200	-1.58676500
C	3.24867400	1.80179300	0.13452500
H	3.30613100	1.56810600	-2.09100800
C	3.86674600	1.05424300	1.17091800
H	5.22524000	-0.72577000	1.09982300
H	2.55819200	2.62688900	0.27306100
H	3.73261000	1.21230800	2.23567900
C	-4.55974100	-0.12922500	0.63047200
C	-4.48410100	-0.20272500	-0.79240900
C	-3.67473700	-1.11045400	1.17082300
H	-5.16014800	0.56927200	1.20108500
C	-3.55111500	-1.22773100	-1.13306700
H	-5.01732900	0.43050900	-1.49157700
C	-3.05309700	-1.78858100	0.08084400
H	-3.48793300	-1.29075900	2.22270000
H	-3.25637700	-1.51462000	-2.13537800
H	-2.31151600	-2.57426000	0.16154300
Fe	2.63101800	-0.26597600	-0.00004000
Fe	-2.61580600	0.24736000	-0.00014300

***C<sub>2</sub>ts Gas Phase***

H	2.48313900	2.88722800	1.33508900
C	1.91776700	2.22089300	0.69985200
C	1.91033900	2.22471900	-0.72289100
C	1.02030600	1.21154700	1.14432700
C	1.00876500	1.21734700	-1.16337200
H	2.46935000	2.89431300	-1.36029500
C	0.48379000	0.53660800	-0.00868700
H	0.80121200	0.97511300	2.17527700
H	0.77848500	0.98696000	-2.19322300
C	-0.48379000	-0.53660800	-0.00868700
C	-1.00876500	-1.21734700	-1.16337200
C	-1.02030600	-1.21154700	1.14432700
C	-1.91033900	-2.22471900	-0.72289100

H	-0.77848500	-0.98696000	-2.19322300
C	-1.91776700	-2.22089300	0.69985200
H	-0.80121200	-0.97511300	2.17527700
H	-2.46935000	-2.89431300	-1.36029500
H	-2.48313900	-2.88722800	1.33508900
C	-0.56520900	4.48784000	-0.77790600
C	-1.55973200	3.51945500	-1.10836900
C	-0.48379000	4.56762500	0.64162400
H	0.02799400	5.05416500	-1.48113700
C	-2.09216100	3.00939200	0.10809100
H	-1.85465000	3.22549800	-2.10517500
C	-1.42775400	3.64919800	1.18868200
H	0.18392700	5.20276600	1.20538800
H	-2.84446400	2.23803200	0.19585800
H	-1.59893200	3.46494000	2.23939800
C	0.48379000	-4.56762500	0.64162400
C	0.56520900	-4.48784000	-0.77790600
C	1.42775400	-3.64919800	1.18868200
H	-0.18392700	-5.20276600	1.20538800
C	1.55973200	-3.51945500	-1.10836900
H	-0.02799400	-5.05416500	-1.48113700
C	2.09216100	-3.00939200	0.10809100
H	1.59893200	-3.46494000	2.23939800
H	1.85465000	-3.22549800	-2.10517500
H	2.84446400	-2.23803200	0.19585800
Fe	-0.00435100	2.62630500	-0.00074200
Fe	0.00435100	-2.62630500	-0.00074200

*C<sub>2</sub>ts CH<sub>2</sub>Cl<sub>2</sub>*

H	2.48011500	2.89115700	1.32328100
C	1.91817000	2.21816700	0.68699600
C	1.90233100	2.22822700	-0.73695300
C	1.02702500	1.20344400	1.13319000
C	1.00219500	1.21905400	-1.17739700
H	2.45007000	2.91027300	-1.37594700
C	0.48586400	0.53428800	-0.02116700
H	0.80942800	0.96302000	2.16653400
H	0.76129800	0.99345200	-2.20887000
C	-0.48586400	-0.53428800	-0.02116700
C	-1.00219500	-1.21905400	-1.17739700
C	-1.02702500	-1.20344400	1.13319000
C	-1.90233100	-2.22822700	-0.73695300
H	-0.76129800	-0.99345200	-2.20887000
C	-1.91817000	-2.21816700	0.68699600
H	-0.80942800	-0.96302000	2.16653400
H	-2.45007000	-2.91027300	-1.37594700



H	-2.48011500	-2.89115700	1.32328100
C	-0.57631100	4.47803500	-0.76733500
C	-1.57144000	3.50779900	-1.09582400
C	-0.48586400	4.55210800	0.65312700
H	0.02068200	5.04181600	-1.47381000
C	-2.09525000	2.99116500	0.12285700
H	-1.86517400	3.20844900	-2.09448700
C	-1.42462500	3.62806100	1.20280900
H	0.19357500	5.17979000	1.21676200
H	-2.84510100	2.21412900	0.21252000
H	-1.58216300	3.43062000	2.25624800
C	0.48586400	-4.55210800	0.65312700
C	0.57631100	-4.47803500	-0.76733500
C	1.42462500	-3.62806100	1.20280900
H	-0.19357500	-5.17979000	1.21676200
C	1.57144000	-3.50779900	-1.09582400
H	-0.02068200	-5.04181600	-1.47381000
C	2.09525000	-2.99116500	0.12285700
H	1.58216300	-3.43062000	2.25624800
H	1.86517400	-3.20844900	-2.09448700
H	2.84510100	-2.21412900	0.21252000
Fe	-0.00715000	2.61744600	-0.00092500
Fe	0.00715000	-2.61744600	-0.00092500

*C<sub>2</sub>ts CH<sub>3</sub>CN*

H	2.47230800	2.89809100	1.33462200
C	1.91478300	2.22077100	0.69819600
C	1.90550700	2.22470300	-0.72623400
C	1.02230400	1.20726400	1.14482600
C	1.00770400	1.21320100	-1.16655500
H	2.45466900	2.90560400	-1.36607300
C	0.48635900	0.53377200	-0.00941000
H	0.79825800	0.97115300	2.17841100
H	0.76979800	0.98296800	-2.19832800
C	-0.48635900	-0.53377200	-0.00941000
C	-1.00770400	-1.21320100	-1.16655500
C	-1.02230400	-1.20726400	1.14482600
C	-1.90550700	-2.22470300	-0.72623400
H	-0.76979800	-0.98296800	-2.19832800
C	-1.91478300	-2.22077100	0.69819600
H	-0.79825800	-0.97115300	2.17841100
H	-2.45466900	-2.90560400	-1.36607300
H	-2.47230800	-2.89809100	1.33462200
C	-0.57007600	4.47327400	-0.77844300
C	-1.56481400	3.50226500	-1.10729400
C	-0.48635900	4.55381400	0.64241400

H	0.03289600	5.03147200	-1.48503500
C	-2.09493900	2.99157000	0.11153700
H	-1.85267500	3.19640000	-2.10625000
C	-1.42883100	3.63301200	1.19191300
H	0.19325600	5.18160500	1.20665800
H	-2.84491200	2.21377900	0.20182100
H	-1.58969700	3.43812400	2.24584100
C	0.48635900	-4.55381400	0.64241400
C	0.57007600	-4.47327400	-0.77844300
C	1.42883100	-3.63301200	1.19191300
H	-0.19325600	-5.18160500	1.20665800
C	1.56481400	-3.50226500	-1.10729400
H	-0.03289600	-5.03147200	-1.48503500
C	2.09493900	-2.99157000	0.11153700
H	1.58969700	-3.43812400	2.24584100
H	1.85267500	-3.19640000	-2.10625000
H	2.84491200	-2.21377900	0.20182100
Fe	-0.00670000	2.61610100	-0.00066800
Fe	0.00670000	-2.61610100	-0.00066800

***C<sub>2h</sub> 2D<sub>5h</sub> Gas Phase***

Fe	-1.74898000	1.95737600	0.00000000
C	-0.04957400	1.58192800	1.15389100
C	0.00455600	0.72271100	0.00000000
C	-0.04957400	2.93331400	0.71145200
C	-0.04957400	2.93331400	-0.71145200
H	-0.06281200	1.25764400	2.18405300
H	-0.07476100	3.80601400	1.34781900
H	-0.07476100	3.80601400	-1.34781900
C	-0.04957400	1.58192800	-1.15389100
H	-0.06281200	1.25764400	-2.18405300
C	-3.55762700	0.84235300	0.00000000
C	-3.49704600	1.67270000	1.15224000
C	-3.40706500	3.02674700	-0.71207300
C	-3.40706500	3.02674700	0.71207300
H	-3.59893000	-0.23783800	0.00000000
H	-3.50964600	1.33774900	2.17925800
H	-3.34123500	3.89782500	-1.34775800
H	-3.34123500	3.89782500	1.34775800
C	-3.49704600	1.67270000	-1.15224000
H	-3.50964600	1.33774900	-2.17925800
C	-0.00455600	-0.72271100	0.00000000
C	0.04957400	-1.58192800	1.15389100
C	0.04957400	-1.58192800	-1.15389100
C	0.04957400	-2.93331400	0.71145200
C	0.04957400	-2.93331400	-0.71145200

Fe	1.74898000	-1.95737600	0.00000000
C	3.49704600	-1.67270000	1.15224000
C	3.40706500	-3.02674700	0.71207300
C	3.40706500	-3.02674700	-0.71207300
C	3.49704600	-1.67270000	-1.15224000
C	3.55762700	-0.84235300	0.00000000
H	3.50964600	-1.33774900	-2.17925800
H	3.34123500	-3.89782500	-1.34775800
H	3.34123500	-3.89782500	1.34775800
H	3.50964600	-1.33774900	2.17925800
H	3.59893000	0.23783800	0.00000000
H	0.06281200	-1.25764400	-2.18405300
H	0.07476100	-3.80601400	-1.34781900
H	0.07476100	-3.80601400	1.34781900
H	0.06281200	-1.25764400	2.18405300

***C<sub>2h</sub> 2D<sub>5d</sub> Gas Phase***

Fe	-1.75797800	1.95092300	0.00000000
C	-0.05754700	1.58188300	1.15388800
C	-0.00020000	0.72241100	0.00000000
C	-0.05754700	2.93305000	0.71105400
C	-0.05754700	2.93305000	-0.71105400
H	-0.07320000	1.25817200	2.18431100
H	-0.08820200	3.80601300	1.34693800
H	-0.08820200	3.80601300	-1.34693800
C	-0.05754700	1.58188300	-1.15388800
H	-0.07320000	1.25817200	-2.18431100
C	-3.51513400	1.06064300	0.71384700
C	-3.47440700	2.41452200	1.15036300
C	-3.47440700	2.41452200	-1.15036300
C	-3.45293800	3.25110700	0.00000000
C	-3.51513400	1.06064300	-0.71384700
C	0.00020000	-0.72241100	0.00000000
C	0.05754700	-1.58188300	1.15388800
C	0.05754700	-1.58188300	-1.15388800
C	0.05754700	-2.93305000	0.71105400
C	0.05754700	-2.93305000	-0.71105400
Fe	1.75797800	-1.95092300	0.00000000
C	3.47440700	-2.41452200	1.15036300
C	3.45293800	-3.25110700	0.00000000
C	3.47440700	-2.41452200	-1.15036300
C	3.51513400	-1.06064300	-0.71384700
C	3.51513400	-1.06064300	0.71384700
H	0.07320000	-1.25817200	-2.18431100
H	0.08820200	-3.80601300	-1.34693800
H	0.08820200	-3.80601300	1.34693800

H	0.07320000	-1.25817200	2.18431100
H	3.39556100	-4.33003700	0.00000000
H	3.44220600	-2.74928100	-2.17743400
H	3.53718800	-0.18865600	-1.35150700
H	3.53718800	-0.18865600	1.35150700
H	3.44220600	-2.74928100	2.17743400
H	-3.44220600	2.74928100	2.17743400
H	-3.39556100	4.33003700	0.00000000
H	-3.44220600	2.74928100	-2.17743400
H	-3.53718800	0.18865600	-1.35150700
H	-3.53718800	0.18865600	1.35150700

*C<sub>i</sub> Gas Phase*

H	-2.71282900	-2.28296400	1.93257200
C	-2.15470600	-1.76209800	1.16817500
C	-2.40898000	-1.80441900	-0.23112700
C	-1.01058600	-0.94633400	1.38536700
C	-1.42322700	-1.01443900	-0.88419200
H	-3.19517500	-2.36260700	-0.71840400
C	-0.57209600	-0.42585500	0.11674000
H	-0.56265400	-0.73502300	2.34524100
H	-1.34486100	-0.86287400	-1.95077500
C	0.57209600	0.42585500	-0.11674000
C	1.01058600	0.94633400	-1.38536700
C	1.42322700	1.01443900	0.88419200
C	2.15470600	1.76209800	-1.16817500
H	0.56265400	0.73502300	-2.34524100
C	2.40898000	1.80441900	0.23112700
H	1.34486100	0.86287400	1.95077500
H	2.71282900	2.28296400	-1.93257200
H	3.19517500	2.36260700	0.71840400
C	-0.46911800	-4.51939300	-0.59227500
C	0.62321500	-3.77634100	-1.13154300
C	-0.31798400	-4.55866100	0.82321400
H	-1.27407500	-4.96604100	-1.15775600
C	1.44697300	-3.36439300	-0.04724800
H	0.79346200	-3.56383900	-2.17691900
C	0.86736300	-3.84069200	1.15902100
H	-0.98907400	-5.03742600	1.52143400
H	2.33882500	-2.75844200	-0.12390900
H	1.24965600	-3.67676600	2.15616800
C	0.46911800	4.51939300	0.59227500
C	0.31798400	4.55866100	-0.82321400
C	-0.62321500	3.77634100	1.13154300
H	1.27407500	4.96604100	1.15775600
C	-0.86736300	3.84069200	-1.15902100

H	0.98907400	5.03742600	-1.52143400
C	-1.44697300	3.36439300	0.04724800
H	-0.79346200	3.56383900	2.17691900
H	-1.24965600	3.67676600	-2.15616800
H	-2.33882500	2.75844200	0.12390900
Fe	-0.51129400	-2.56943700	0.16946200
Fe	0.51129400	2.56943700	-0.16946200

***C<sub>1</sub> 2D<sub>5d</sub> Gas Phase***

Fe	2.61575800	0.24308200	0.00001700
C	1.16343800	1.16041700	-1.15987700
C	0.56214900	0.54846400	-0.00001300
C	2.08283300	2.14216100	-0.71248700
C	2.08280600	2.14207800	0.71269200
H	0.95512200	0.91774900	-2.19194900
H	2.70481600	2.75833800	-1.34521900
H	2.70478800	2.75818000	1.34550000
C	1.16342200	1.16026600	1.15995100
H	0.95509800	0.91748700	2.19199500
C	3.24459200	-1.61268300	-0.71390200
C	4.14145600	-0.59966600	-1.15263200
C	4.14159400	-0.59930200	1.15269000
C	4.69211200	0.03096500	-0.00010800
C	3.24469200	-1.61246500	0.71437600
C	-0.42530200	-0.50625900	-0.00008200
C	-1.05302600	-1.09767000	-1.14672000
C	-1.05304100	-1.09780100	1.14647500
C	-1.96159600	-2.10569400	-0.71265800
C	-1.96160400	-2.10577400	0.71228600
Fe	-2.63781400	-0.26953200	-0.00009300
C	-4.24234100	0.56902100	-1.14918900
C	-4.80551900	-0.04609500	0.00015000
C	-4.24210100	0.56904300	1.14935700
C	-3.34017500	1.58408100	0.71320200
C	-3.34032100	1.58406900	-0.71323900
H	-0.84589700	-0.84197900	2.17545500
H	-2.55058400	-2.74627800	1.35304800
H	-2.55056000	-2.74613500	-1.35349800
H	-0.84585400	-0.84174200	-2.17566900
H	-5.50305600	-0.87180200	0.00023100
H	-4.45308200	0.30467200	2.17588100
H	-2.75981400	2.23568000	1.35032200
H	-2.76010400	2.23567100	-1.35048800
H	-4.45355400	0.30464600	-2.17566500
H	4.34884400	-0.33504400	-2.17957400
H	5.39054500	0.85524200	-0.00027500

H	4.34909900	-0.33437700	2.17953100
H	2.66170700	-2.26256500	1.35110100
H	2.66154100	-2.26297600	-1.35036800

***C<sub>1</sub> ID<sub>5d</sub> ID<sub>5h</sub> Gas Phase***

Fe	-2.61403600	0.24431200	0.00008900
C	-1.17416200	1.17802600	1.15953200
C	-0.56649900	0.57185500	-0.00036700
C	-2.10659500	2.14768600	0.71132900
C	-2.10669000	2.14657500	-0.71428800
H	-0.96035200	0.94090400	2.19174100
H	-2.73325200	2.75921000	1.34384900
H	-2.73333400	2.75720300	-1.34768500
C	-1.17441200	1.17615900	-1.16109000
H	-0.96035500	0.93769100	-2.19293200
C	-3.05970400	-1.79441900	0.00442800
C	-3.61980800	-1.16969700	1.15594600
C	-4.52535000	-0.16895700	-0.71394300
C	-4.52759500	-0.16549900	0.71023000
H	-2.32567900	-2.58796700	0.00754700
H	-3.39385800	-1.40945300	2.18490400
H	-5.09840900	0.48966000	-1.35051000
H	-5.10263000	0.49618600	1.34180900
C	-3.61610900	-1.17523700	-1.15191500
H	-3.38695500	-1.42000500	-2.17898000
C	0.41958900	-0.48460100	0.00000800
C	1.04415600	-1.07942700	1.14682400
C	1.03992000	-1.08503700	-1.14637900
C	1.94239900	-2.09577200	0.71462000
C	1.93720500	-2.10090000	-0.70950600
Fe	2.63563000	-0.26515900	-0.00582600
C	4.24022100	0.55352200	1.15322900
C	4.80544400	-0.06486100	0.00718000
C	4.25331700	0.55361600	-1.14534000
C	3.35724400	1.57757000	-0.71329900
C	3.34676600	1.57590500	0.71409500
H	0.83145300	-0.83279700	-2.17593100
H	2.51822300	-2.74971300	-1.34930300
H	2.52758300	-2.73942500	1.35566700
H	0.84111500	-0.81806900	2.17526800
H	5.49479600	-0.89749000	0.01133300
H	4.46836500	0.28792400	-2.17066600
H	2.78675200	2.23432700	-1.35405000
H	2.76742400	2.23060800	1.34890200
H	4.44163400	0.28419800	2.18045100

***C<sub>1ex</sub> Gas Phase***

H	2.57896100	-2.76428100	1.34451500
C	1.98104400	-2.12732700	0.70882800
C	1.97978200	-2.12436600	-0.71787600
C	1.07515700	-1.11582100	1.14704000
C	1.07342800	-1.11131800	-1.15023100
H	2.57705000	-2.75820000	-1.35726200
C	0.46238500	-0.50180400	0.00015000
H	0.87981700	-0.85653200	2.17740300
H	0.87621300	-0.84820600	-2.17923600
C	-0.53367300	0.55085900	0.00045400
C	-1.13182300	1.16043200	-1.16030900
C	-1.13395100	1.16354600	1.15867000
C	-2.05898300	2.13837400	-0.71582600
H	-0.91965000	0.91890100	-2.19196000
C	-2.06029800	2.14045500	0.70941700
H	-0.92371400	0.92454400	2.19133800
H	-2.68040700	2.75264000	-1.35082700
H	-2.68288500	2.75655900	1.34150600
C	4.50750200	0.21774300	-0.80194800
C	3.55654200	1.24173700	-1.10659900
C	4.60075700	0.11347700	0.61560400
H	5.04409300	-0.38463700	-1.52060700
C	3.06510800	1.77359900	0.12122500
H	3.24656900	1.54370300	-2.09661700
C	3.70526200	1.07036100	1.18582000
H	5.21916800	-0.58300600	1.16294800
H	2.31210200	2.54084800	0.22668500
H	3.52780800	1.22045600	2.24107700
C	-4.53137100	-0.12072800	0.63831200
C	-4.46125800	-0.20161400	-0.78186400
C	-3.65240500	-1.10292500	1.18054300
H	-5.13207100	0.57593900	1.20499600
C	-3.53739300	-1.23231000	-1.12046600
H	-4.99987200	0.42297100	-1.47989100
C	-3.04042800	-1.79021000	0.09336600
H	-3.47595400	-1.28586500	2.23067300
H	-3.26157600	-1.53370200	-2.12068300
H	-2.31346600	-2.58603000	0.17505800
Fe	2.61912500	-0.27815600	-0.00053200
Fe	-2.58314400	0.24319100	-0.00042900

### Potential energy surfaces and vibronic modes for MV $\mathbf{BF}^+$ .

Within the borders of PKS model the *overall* vibrational modes of interest couple vibrational modes that are centered on both metal centers. In particular, in the case of the MV  $\mathbf{BF}^+$  cation, these new coordinates take the following form:<sup>1</sup>

$$Q_{\pm} = 2^{-1/2}(Q_{\text{FeII}} \pm Q_{\text{FeIII}}) \quad (1)$$

where  $Q_{\text{FeII}}$  and  $Q_{\text{FeIII}}$  are stretches localized on  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  centers, respectively. The symmetric combination gives the symmetric stretch and the antisymmetric combination gives the antisymmetric stretch. It was first suggested that, within the PKS model, the symmetric stretch did not significantly contribute to the electron transfer process and thus it can be disregarded in vibronic coupling analyses, while only the antisymmetric stretch,  $Q_{-}$ , should be retained. However, Hush<sup>2</sup> has shown that the symmetric stretch is indeed important and should be considered in the analysis of spectral properties of  $\mathbf{BF}^+$ . Again, analyses of MV systems in the context of DFT have focused largely on class III compounds such as the Creutz-Taube ion,<sup>3</sup>  $[\text{Fe}_2(\text{OH})_3(\text{NH}_3)_6]^{2+}$ , and  $[\text{Mn}_2(\text{O})_2(\text{NH}_3)_8]^{3+}$ .<sup>4</sup> These investigations include PES analyses of both the symmetric and antisymmetric stretches, and have successfully reproduced the quadratic, single-welled behavior of the class III complexes as well as the double-welled character of the class II complexes. The vibrations considered in the usual vibronic coupling analyses of the MV complexes are normal modes in which various bond lengths are lengthened or shortened and then frozen while the rest of the molecule optimizes (a so-called *relaxed* scan of the PES). *Rigid* scans can also be created where the identical bond length changes are made as in the *relaxed* scan, but the rest of the molecule does not undergo relaxation, or a partial optimization. In the creation of PESs for high symmetry complexes such as the Creutz-Taube ion, there is certainty that the true symmetric and antisymmetric stretches are being used. However, in the case of  $\mathbf{BF}^+$  the



antisymmetric and symmetric stretches are difficult to define due to the fact that, in the  $C_1$  point group, all molecular vibrations will couple to one another.

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- (1) (a) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996 (b) Wong K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369.
- (2) Reimers, J. R.; Hush, N. S. *Chem. Phys.*, **1996**, *208*, 177.
- (3) Bencini, A; Gatteschi, D; Mattesini, M; Totti, F.; Cofini, I. *Mol. Cryst. And Liq. Cryst.*, **1999**, *335*, 665.
- (4) (a) Bencini, A.; Ciofini, I.; Daul, C. A.; Ferretti, A. *J. Am. Chem. Soc.* **1999**, *121*, 11418. (b) Chen, Z.; Bian, J.; Zhang, L.; Li, S. *J. Chem. Phys.*, **1999**, *111*(24), 10926.